



Activated carbon supported metal catalysts for reduction of nitrate in water with high selectivity towards N_2



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ABSTRACT

The catalytic removal of nitrate in water with hydrogen was investigated by using different activated carbon-supported metal catalysts. A commercial activated carbon (CAC) and one prepared by chemical activation of grape seeds with phosphoric acid (GS) were evaluated for the preparation of bimetallic catalysts (Pd–Cu, Pd–Sn and Pd–In). The support plays an important role in the catalytic performances for nitrate removal, affecting both activity and selectivity. Pd–Cu catalyst supported on GS showed the highest nitrate removal activity and nitrite was not found as by-product. The acidity of the reaction medium is associated with this behavior, attributing this effect to the chemical composition of the catalyst support. Control of pH through CO_2 addition to the reaction medium was beneficial in the case of the Pd–Cu catalyst prepared with CAC. However, no significant influence was observed in the case of the GS-supported catalyst. The concentration of promoting metal affects more strongly the catalyst performance than that of Pd. Low Cu contents (0.5 and 1.5 wt.%) within the range tested (0.5–5 wt.%) led to the highest selectivity towards the undesired ammonium ion. The catalysts supported on GS with 2.5% Cu and 5% Pd allowed achieving the European Standards for drinking water when a 100 mg/L nitrate starting solution was treated, in terms of nitrate, nitrite and ammonium concentrations. The Pd-based bimetallic catalysts containing Sn and In as promoting metal showed a lower catalytic activity and significantly higher selectivity towards ammonium.

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1. Introduction

The concentration of nitrate in the soil, and subsequently in ground and surface water has become a severe problem throughout the world. Man-made or man-induced sources of nitrogen introduction in the environment include agricultural fertilizers, septic tank systems and animal waste disposal [1]. As the most evident effect, nitrate can cause eutrophication disrupting normal ecosystems of rivers and lakes [2]. In addition, nitrate is reduced in the human body, being responsible for methemoglobinemia and possibly a precursor of carcinogenic nitrosamine [3]. The European Community has set the maximum levels of nitrate and nitrite in drinking water at 50 and 0.5 mg/L, respectively [4]. The US Environmental Protection Agency has proposed 10 mg/L of nitrate as a guide level for drinking [5]. Thus, there is a need to develop water treatment methods involving conversion of nitrates into innocuous N_2 . The catalytic reduction of nitrates with hydrogen appears as a promising solution for the removal of nitrates from water. The most widely accepted reaction scheme for denitration consists of a

complex pathway with nitrate reduction to nitrite in a first stage and then to gaseous nitrogen or ammonium and hydroxide ions, probably through the formation of N_2O as an intermediate. Ammonium can be considered as an undesirable by-product, whose maximum allowable concentration in drinking water is fixed at 0.5 mg/L.

Substantial efforts have been made to prepare and optimize catalysts for aqueous-phase nitrate removal. It has been shown that monometallic catalysts based on precious metals such as Pd, Pt, Rh or Ir deposited on non-reducible supports have a low activity in the reduction of nitrate [6–10]. The effective reduction of nitrate requires the combination of noble metals with at least a second metal [11]. Bimetallic catalysts based on Pd have shown higher nitrate conversion, whereas those prepared with Pt are more selective for the reduction to N_2 [12,13]. Copper has been frequently used as second or promoting metal [2,6,10] but other suitable promoters such as Sn, Ni, Fe, Ag, Zn, In or Zn have demonstrated interesting possibilities [10,14–19]. Although some aspects of nitrate reduction with H_2 are not well established, it is widely accepted that the promoting metal is responsible for the redox reaction and it remains in metallic state thanks to the spill-over of hydrogen from the precious metal. Some works have concluded that the activity and selectivity of the bimetallic catalysts are

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Table 1
Nomenclature of the catalysts prepared.

Catalyst	Activated carbon support	Pd (wt. %)	Cu (wt. %)	Sn (wt. %)	In (wt. %)
5Pd–2.5Cu/CAC	Merck	5	2.5	–	–
5Pd–2.5Cu/GS	Grape seeds	5	2.5	–	–
5Pd–0.5Cu/GS	Grape seeds	5	0.5	–	–
5Pd–1.5Cu/GS	Grape seeds	5	1.5	–	–
5Pd–5Cu/GS	Grape seeds	5	5	–	–
0.5Pd–2.5Cu/GS	Grape seeds	0.5	2.5	–	–
1.5Pd–2.5Cu/GS	Grape seeds	1.5	2.5	–	–
2.5Pd–2.5Cu/GS	Grape seeds	2.5	2.5	–	–
0.5Pd–0.25Cu/GS	Grape seeds	0.5	0.25	–	–
1Pd–0.5Cu/GS	Grape seeds	1	0.5	–	–
5Pd–2.5Sn/GS	Grape seeds	5	–	2.5	–
5Pd–2.5In/GS	Grape seeds	5	–	–	2.5

sensitive to the metals ratio, there is no general agreement in this respect. Several works [17,20–22] showed that the activity of the Pd–Cu catalysts goes through a maximum at Pd/Cu ratios around 2, whereas, other works established optimum catalytic activity at Pd/Cu ratios between 0.6 and 1 [12,13,23].

Different supports have been used for the preparation of denitration catalysts, such as activated carbon [9,10,23], alumina [17,24–26], ceria [27–29], titania [22,30,31], niobia [1] and calcined hydrothermal-type materials [32–34]. Metals supported on activated carbon showed high selectivity to N_2 , which has been attributed to high surface area allowing higher metals dispersion [9,13]. A key parameter in denitration is pH, since the reduction of nitrate leads to the formation of hydroxide ion, increasing the pH of the reaction medium up to 10. This value is unacceptable for drinking water and induces a decrease of both the activity and the selectivity towards N_2 [10,35]. Different strategies have been developed to control the pH, the most common being the addition of HCl, HCOOH or CO_2 in the reaction media [11,35–37]. Thus, for example, the continuous addition of CO_2 can neutralize hydroxide ions, leading to a decrease of ammonium formation without significantly affecting the catalytic activity [14,15]. In addition to this, the control of pH becomes necessary for minimizing Cu leaching, as it was reported in a previous work, where Cu leaching reached a minimum when the reaction medium was buffered at pH 6 [10]. The acid-base character of the support can be also tailored for the sake of improving the catalyst performance [38].

The aim of this work is to study the catalytic reduction of nitrate from aqueous solutions using hydrogen with different bimetallic catalysts supported on different activated carbons, checking both nitrate conversion and selectivity to reaction products. The discussion is focused on the role of the metallic combinations, metals ratios, support and pH.

2. Experimental

2.1. Materials

Two activated carbons were used as supports: a commercial activated carbon (CAC) supplied by Merck and an own-made activated carbon (GS) prepared in our lab by chemical activation of grape seeds with phosphoric acid. Grape seeds were pretreated with 5 vol.% sulfuric acid for 24 h in order to remove oils and improve wettability. Then, they were rinsed with water until neutrality and absence of sulfate in the liquid phase, dried overnight at 120 °C and stored for further activated carbon preparation. Pretreated seeds were impregnated with 7.7 M phosphoric acid solution at 85 °C for 2 h under stirring (150 rpm). After impregnation the sample was dried overnight at 120 °C. Carbonization of impregnated sample was carried out in a vertical quartz-tube furnace (4.8 cm i.d., 50 cm length) at 500 °C for 2 h under a continuous nitrogen flow of 100 NmL/min. The activation temperature was

reached at 10 °C/min heating rate. Finally, the carbonized sample once cooled under N_2 flow was washed with water under reflux for 12 h.

2.2. Catalyst preparation and characterization

The bimetallic catalysts were prepared by incipient wetness impregnation of the CAC or the GS with an average particle diameter of 1.5 and 3 mm, respectively. Different combinations of Pd with Cu, Sn or In with nominal loadings between 0.5 and 5 wt.% were used as active phases. The impregnation was carried out with a volume of solution of the precursor salts ($PdCl_2$, $CuCl_2 \cdot 2H_2O$, $InCl_3$ and $SnCl_4$) exceeding by 30% the total pore volume of the activated carbon. Impregnation was followed by drying at room temperature for 2 h and overnight at 60 °C. Finally, the samples were calcined in air atmosphere at 200 °C and reduced in H_2 atmosphere at 500 °C with a flow rate of 60 NmL/min. The nomenclature and metallic content of the catalysts are shown in Table 1.

The porous structure of the activated carbons and the catalysts was characterized by N_2 adsorption–desorption at 77 K (Autosorb-1 Quantachrome). The BET equation was used to obtain the surface area and the t -method for micropore volume. The external area or non-micropore surface area was calculated as the difference between the BET surface area and the micropore surface area. The difference between the volume of N_2 adsorbed at 0.95 relative pressures (as liquid) and the micropore volume was taken as the mesopore volume. The metal content of the catalysts was analyzed by total reflection X-ray fluorescence, using a TXRF EXTRA II spectrometer.

The amount of oxygen surface groups of the supports was determined by temperature programmed desorption (TPD), heating 0.1 g of the AC sample up to 1100 °C in a vertical quartz tube under continuous N_2 flow of 1 NL/min at a heating rate of 10 °C/min. The evolved amounts of CO and CO_2 were analyzed by means of a non-dispersive infrared absorption analyzer (Siemens, model Ultramat 22).

Scanning electron microscopy (SEM) micrographs were obtained with a JEOL 5800 scanning microscope. This technique coupled with an energy-dispersive X-ray spectrometer (INCAx-sight) allowed obtaining chemical analysis of the catalysts (SEM-EDX). The particle size distribution of the metallic phase was determined by transmission electron microscopy (TEM) using a JEOL 2100UHR microscope coupled with an energy-dispersive X-ray spectrometer (INCAx-sight) used for chemical elemental analysis. Samples were prepared placing a drop of a suspension of catalyst dispersed in ethanol onto a carbon-coated Ni grid and leaving it dry at room temperature. Software 'ImageJ 1.44i' was used for counting and measuring metal particles on digital TEM images (more than 200 nanoparticles were measured per image). Surface-area-weighted mean diameters (d_s) were calculated as $d_s = \sum n_i d_i^3 / \sum n_i d_i^2$, where n_i is the number of metal particles of

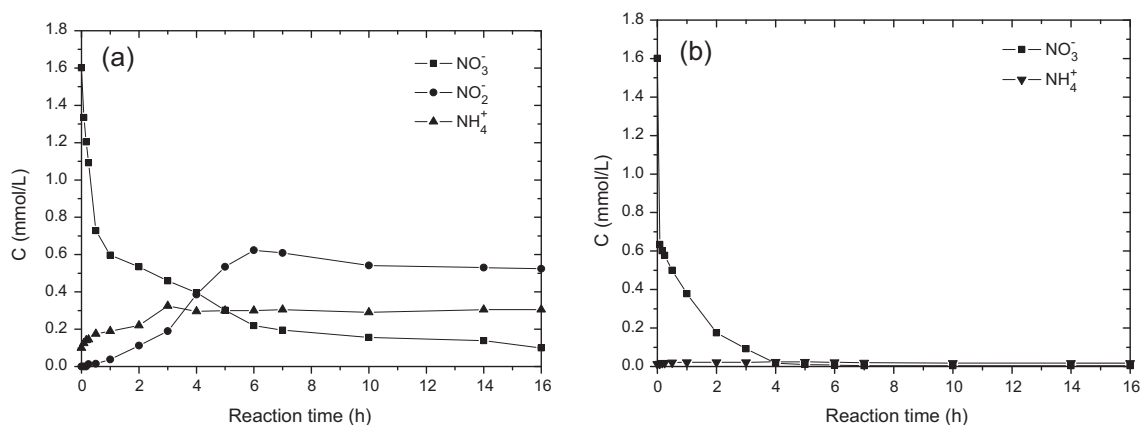


Fig. 1. Catalytic reduction of NO_3^- with H_2 using (a) 5Pd–2.5Cu/CAC and (b) 5Pd–2.5Cu/GS catalysts ($T = 30^\circ\text{C}$).

a given diameter d_i , as described elsewhere [39]. The number of exposed metal atoms (D , %) was calculated assuming spherical shape of the metal particles as $D = [(6 \cdot 10^9 V_M)/(A_M \cdot d_s)] \cdot 100$, where V_M is the bulk atomic volume of the metals (cm^3) and A_M is the area of an atom (cm^2) [40].

2.3. Nitrate reduction experiments

Nitrate reduction reactions were performed with 100 mL of $1.6 \cdot 10^{-3}$ mol/L sodium nitrate aqueous solutions (100 mg/L) in a semi-batch reactor at atmospheric pressure and 30°C under continuous H_2 flow (250 N mL/min). The catalyst (0.5 g) was reduced before reaction at 120°C for 1 h with a flow rate of 250 N mL/min of H_2 , then 90 mL of degassed ultra pure water at 30°C was added. The catalyst was maintained under bubbling of hydrogen for 10 min before introduction of the reactant. The catalyst dispersion in the aqueous medium was operated by the H_2 bubbling flow through a porous glass located at the bottom of the reactor. Gas bubbling provided convenient agitation of the reaction medium. In some experiments, CO_2 was introduced to the reaction media for buffering the solution at a pH value around 6. In the rest of experiments the initial pH of the reaction medium was mainly determined by the acidity of the catalysts (e.g. 4.2 and 6.7 for 5Pd–2.5Cu/GS and 5Pd–2.5Cu/CAC, respectively) and it increased as the reduction of nitrate took place. Samples were periodically taken, immediately filtrated and then the liquid phase was analyzed.

Nitrate and nitrite concentrations were analyzed by high performance liquid chromatography (HPLC) using a C_{18} column at $\lambda = 210$ nm with a UV detector. Ammonium ion was quantified using an Alltech Universal Cation column coupled with a conductivity detector. The oxalic acid used as acidic mobile phase provided the complete conversion of the ammonia in the basic form into ammonium ions. The amount of N_2 formed was calculated as the difference between the inlet nitrate concentration and the sum of the nitrate, nitrite and ammonium concentration in the effluent. Nitrate, nitrite and ammonium adsorption test indicated negligible uptake of these ions by the catalytic supports catalysts are compared as a function of their conversion and their selectivity towards reaction products. The selectivity to nitrite, ammonium and N_2 are defined as:

$$S_{\text{NO}_2^-}(\%) = \frac{C_{\text{NO}_2^-}}{C_{\text{NO}_3^-} - C_{\text{NO}_3^-}} \cdot 100 \quad (1)$$

$$S_{\text{NH}_4^+}(\%) = \frac{C_{\text{NH}_4^+}}{C_{\text{NO}_3^-} - C_{\text{NO}_3^-}} \cdot 100 \quad (2)$$

$$S_{\text{N}_2}(\%) = 100 - S_{\text{NO}_2^-} - S_{\text{NH}_4^+} \quad (3)$$

where $C_{\text{NO}_2^-}$ and $C_{\text{NH}_4^+}$ are respectively the nitrite and ammonium concentration (mmol/L) at time t .

3. Results and discussion

3.1. Effect of the support

Fig. 1 shows the results obtained with Pd–Cu catalysts supported on two different activated carbons (CAC and GS) with the same total metal content (7.5 wt.%) and the same Pd/Cu mass ratio (2). The 5Pd–2.5Cu/GS catalyst showed a significantly higher activity for nitrate reduction achieving a complete conversion of nitrate after 4 h. In the case of 5Pd–2.5Cu/CAC catalyst the nitrate conversion reached around 60% upon the same reaction time and roughly exceeded 80% doubling that reaction time.

Significant differences in selectivity were also observed, the 5Pd–2.5Cu/GS catalyst showing a much better performance on that respect since nitrite was not detected among the reaction products and the amount of ammonium produced was much lower. The catalyst 5Pd–2.5Cu/GS maintained its activity during the whole reaction cycle, thus leading to total conversion of nitrate. Therefore, no significant loss of active phase by leaching is expected.

The porous structure of the activated carbons used as supports and the two catalysts prepared are reported in Table 2. Some important differences can be observed between the two starting activated carbons. The own prepared activated carbon from GS shows a higher BET surface area accompanied by a significantly higher contribution of mesoporosity, so that the external or non-microporous surface area represents almost 25% of the BET surface area, whereas that percentage is less than 2% in the case of the commercial activated carbon. Nevertheless, the introduction of the active metals reduces significantly the BET surface area, external area and the mesopore volume of the catalysts. That decrease was more pronounced in the case of 5Pd–2.5Cu/GS catalyst, leading to more similar porous structures for both catalysts. Although the difference in external area is still significant, the porous structure of the catalysts cannot explain alone the significantly different behavior of the two catalysts.

Barrabes et al. [28] have explained the differences found between Pt/CeO₂ catalysts tested in nitrate reduction on the basis of both metal particle size and dispersion. To check the influence of this factor in our case TEM characterization was carried out. The results are summarized in Table 3, showing that no significant difference was found between the 5Pd–2.5Cu/GS and 5Pd–2.5Cu/CAC

Table 2
Porous structure of the activated carbon and catalysts prepared.

Sample	S_{BET} (m ² /g)	A_{ext} (m ² /g)	$V_{\text{micropore}}$ (cm ³ /g)	V_{mesopore} (cm ³ /g)
GS	1139	269	0.49	0.24
CAC	933	18	0.38	0.16
5Pd–2.5Cu/CAC	497	8	0.26	0.02
5Pd–2.5Cu/GS	400	32	0.20	0.02
5Pd–0.5Cu/GS	685	34	0.35	0.03
5Pd–1.5Cu/GS	600	32	0.32	0.03
5Pd–5Cu/GS	362	31	0.18	0.02

Table 3
Dispersion (D) and mean metal particle size (dp) of the catalysts as obtained from TEM.

Sample	TEM	
	D (%)	dp (nm)
5Pd–2.5Cu/CAC	9	11.7
5Pd–2.5Cu/GS	11	10.2
5Pd–0.5Cu/GS	10	11.2
5Pd–1.5Cu/GS	10	11.0
5Pd–5Cu/GS	10	11.0
0.5Pd–2.5Cu/GS	27	4.1
1.5Pd–2.5Cu/GS	24	4.6
2.5Pd–2.5Cu/GS	21	5.2
5Pd–2.5Sn/GS	5	22.3

catalysts. TEM micrographs of the two catalysts show that most of the particles have a pseudo-spherical morphology.

A key parameter in water denitration is the pH of the reaction medium. The pH values measured at the end of the experiments of Fig. 1 were 6.6 and 8.9 for 5Pd–2.5Cu/GS and 5Pd–2.5Cu/CAC catalysts, respectively. The nitrate conversion was higher with the first one, with a decreased release of hydroxide ions, which suggests a buffering effect of the catalyst neutralizing the OH[−] generated upon the process that can be attributed to its chemical composition. Chemical characterization by X-ray fluorescence (Table 4) shows a good agreement between the nominal and measured metal loads of the catalysts indicating that most of the metal from the precursor salt solutions was retained on the activated carbon supports. Likewise, the chemical characterization indicates an important percentage of phosphorous (around 5 wt.%) in the catalyst whose activated carbon support was prepared by H₃PO₄ activation of grape seeds. The presence of P in this catalyst was confirmed by SEM-EDS (Fig. 2). Since the GS activated carbon was exhaustively washed until neutrality after chemical activation with phosphoric acid, most of the phosphorous detected must be included into the activated carbon matrix. This important phosphorous content could play some role on the superior activity and selectivity of the GS supported catalyst with respect to the one prepared with the

Table 4
Results obtained by X-ray fluorescence analysis of the catalysts.

Concentration (%)	5Pd–2.5Cu/GS	5Pd–2.5Cu/CAC
Pd	5.2	5.0
Cu	2.2	2.8
P	5.0	–
Si	22.5	28.9
S	–	0.2
Fe	0.01	0.03
Ni	8.4×10^{-4}	5.2×10^{-4}
Ti	5.0×10^{-3}	0.018
Ca	0.15	0.014
Ar	0.31	0.34
Sr	6.0×10^{-3}	8.6×10^{-4}
Zn	2.1×10^{-3}	7.7×10^{-4}
Br	9.8×10^{-4}	1.3×10^{-3}
Cl	3.6	2.5
Mo	–	0.2

commercial activated carbon (CAC) where no P was detected. Moreover, it should be noticed that the 5Pd–2.5Cu/CAC catalyst show a 0.2 wt.% sulfur content, resulting from the chemical composition of CAC. Although sulfur has been described as a poison for metal catalysts, the sulfur in CAC is expected to be closely linked and embedded in the carbon turbostratic structure with a low mobility and reactivity that can lead to interaction with activated phase.

The two catalysts tested showed also differences in the pH of the aqueous slurry and the TPD profiles, which are associated to the nature and amount of surface oxygen groups (SOG). On the one hand, the pH of the slurry was 3.6 and 6.5 for 5Pd–2.5Cu/GS and 5Pd–2.5Cu/CAC, respectively. On the other hand, the GS activated carbon showed a TPD profile with a much higher amount of CO and CO₂-evolving groups (2406 μmol/g) than CAC (984 μmol/g). Carboxylic acids and lactone groups are known to evolve as CO₂ upon heating and carboxylic anhydride produces both CO₂ and CO, whereas CO derives from phenols, ethers, carbonyls, and quinones. The overall amount of CO₂ evolved from the two supports was so similar. However, the CO evolved from the oxygen surface groups of the GS activated carbon may be attributed to the higher presence of phenols. Moreover, it has been reported that chemical activation with phosphoric acid results in carbons with high thermal stability surface groups that provide high surface acidity [41,42]. These groups decompose at temperatures higher than 700 °C yielding CO and CO₂. The GS catalyst is mainly characterized by a considerable amount of CO desorbed at high temperatures ($T > 750$ °C) upon TPD that might be partly due to the decomposition of stable C–O–P groups. Therefore, the GS support has a more acidic character due to the groups formed upon the activation of grape seeds with H₃PO₄ and this may also play some role in the performance of the catalyst prepared with such support. Most of the catalysts based in Pd–Cu reported in the literature led to the formation of nitrites during nitrate reduction [6,12], therefore, a support with such a higher concentration of acidic sites as GS may accelerate the disappearance of nitrite, since it has been reported that nitrite generation was not observed in acidic medium when using formic acid as reducing agent [35]. In fact, Centi and Perathoner [43] demonstrated that nitrite formation decreases with the pH, and that below pH 3 this species does not appear as reaction by product.

To lean more on the reaction pathway with the two catalysts tested, some experiments of nitrite reduction were carried out. Fig. 3 shows the results obtained. Complete disappearance of nitrites was observed in less than 4 h with the 5Pd–2.5Cu/GS catalyst, while only a 75% conversion was achieved after 6 h reaction with the 5Pd–2.5Cu/CAC catalyst. Matatov-Meytal et al. [44] obtained results fairly similar to ours with the 5Pd–2.5Cu/CAC catalyst. They concluded that the occurrence of catalyst deactivation or reaction inhibition was caused by an increase in pH. In the case of our 5Pd–2.5Cu/GS catalyst the acidity provided by the support seems to play an important role on the excellent behavior of that catalyst relative to nitrite formation.

Recent works [45,46] have shown that the activation with phosphoric acid of lignocellulosic materials lead to the formation of stable C–O–PO₃ and (C–O)₃PO groups with acidic character, as well as C₃PO and C₃P surface phosphate groups and polyphosphate

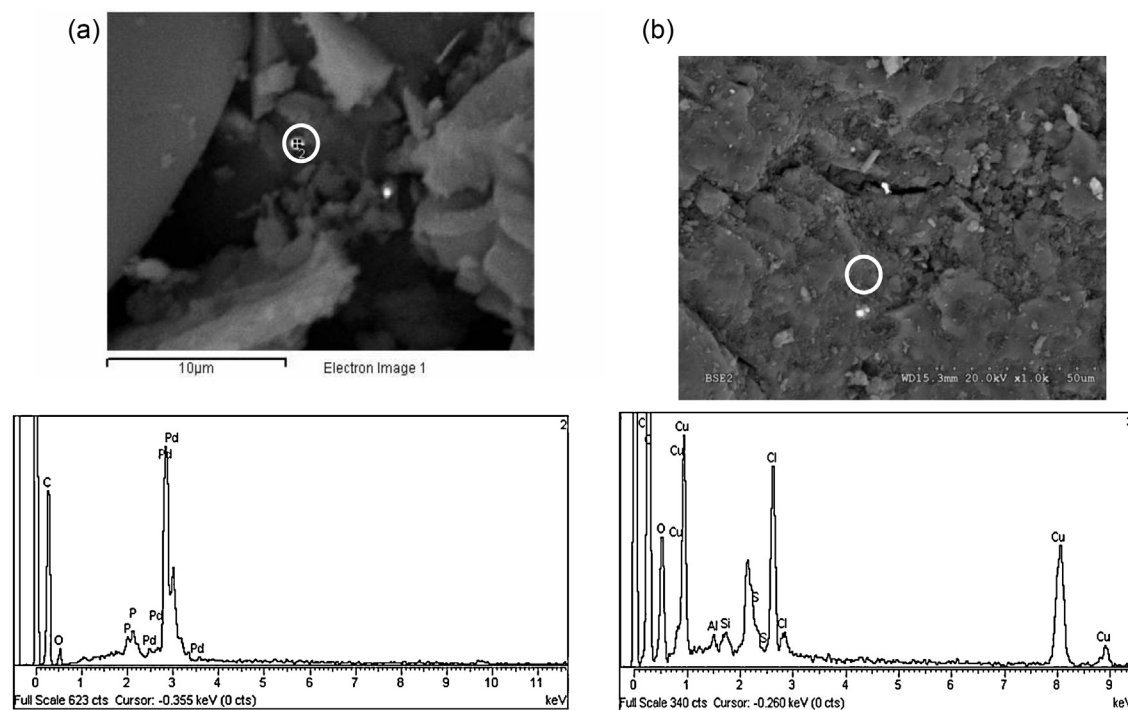


Fig. 2. SEM-EDS analyses of (a) 5Pd-2.5Cu/CAC and (b) 5Pd-2.5Cu/GS catalysts.

groups on the surface of activated carbons. These groups have an important role in both the resistance of the carbon surface to oxidation, changing the oxidation mechanism, and in the catalysis of reactions such as the dehydration of ethanol to ethylene.

Since, the catalytic activity and selectivity in denitration seems to be influenced by pH and this changes during the reaction, we performed some experiments under controlled pH by continuously bubbling CO_2 into the reaction solution at a 150 NmL/min flow-rate. Compared to un-buffered runs the addition of CO_2 to the reaction medium seems to be beneficial for the denitration process looking at both, nitrate conversion and the selectivity towards nitrite and ammonium, which were significantly improved for the CAC-supported catalyst, as can be seen in Fig. 4. Thus, when the solution was buffered with CO_2 , the conversion was improved from 76% to 88% and the selectivity towards N_2 at the end reaction time increased from 20% to 60%, due to the decrease in both nitrite and ammonium generation. This effect of buffering has been reported in

most of the works in the literature, although Gao et al. [22] showed that the addition of CO_2 provided a high selectivity towards N_2 but not an increase of the catalytic activity for titania supported Pd-Cu catalysts. Virtually no influence of the addition of CO_2 was observed with the 5Pd-2.5Cu/GS catalyst which already provided excellent results in the non-buffered experiments. However, the profile of the evolution of nitrate was slightly different, yielding a faster conversion between the first and third hours. It can be inferred that tailoring the acidity of the reaction sites of the catalyst is more efficient than buffering the reaction medium, since mass transport restrictions to the reaction sites are lower.

3.2. Effect of total metal content and Pd/Cu ratio

The influence of total metal (Pd-Cu) content and Pd/Cu ratio in both the catalytic activity and selectivity was investigated with different catalysts prepared using the GS activated carbon as support. Firstly, the Pd/Cu mass ratio was varied fixing the Pd content at 5 wt.%. As shown in Fig. 5, low copper values (0.5–1.5 wt.%) were not beneficial neither for nitrate conversion nor for selectivity towards N_2 . The best performance was observed for 2.5 wt.% Cu. The lower selectivity to ammonium of 5Pd-2.5Cu/GS catalyst can be observed in the whole range of nitrate conversion, as shown in Fig. 6. These results suggest that the active atomic arrangement, particle size and its distribution, morphology and electrodeposited/metallic species ratio of the active phase can have a crucial influence in the removal of nitrate, rather than the metal loading.

As can be seen in Table 2, the textural properties of the catalysts are affected by the incorporation of the metallic phases (Pd and Cu). A monotonical decrease in BET surface area takes place as the total metal content is increased. Nevertheless, as indicated before, it is important to look at the changes occurring in the size of the metallic phase. The results of Table 3 show no significant differences in the mean particle size for the catalyst with 5 wt.% Pd and different Cu loads. Thus, the differences in activity have been interpreted in previous works in the literature in terms of the different locations on active phase: edge and corner sites vs terraces

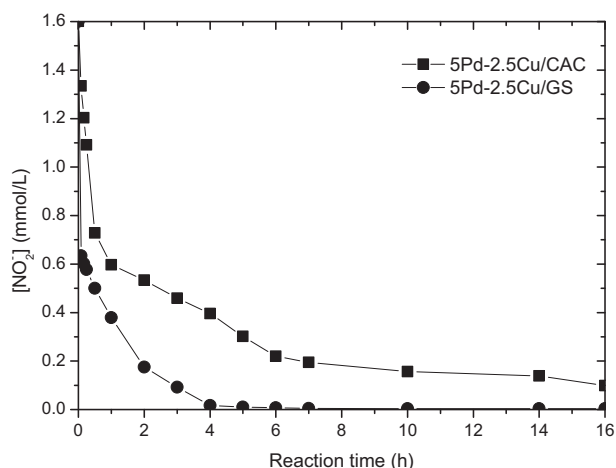


Fig. 3. Nitrite reduction with 5Pd-2.5Cu/CAC and 5Pd-2.5Cu/GS catalysts ($T = 30^\circ\text{C}$).

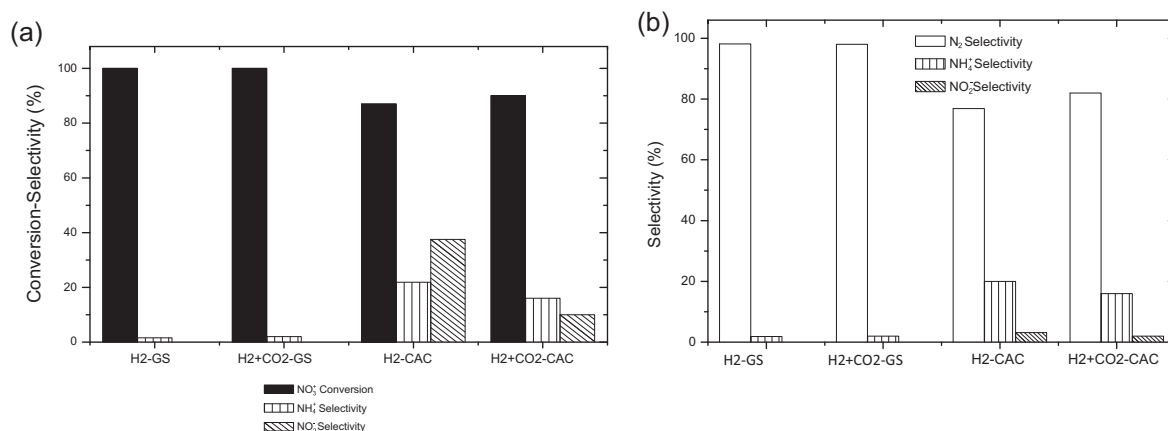


Fig. 4. Nitrate conversion and products selectivity (a) at reaction time = 8 h and (b) selectivity at 50% nitrate conversion with 5Pd–2.5Cu/CAC and 5Pd–2.5Cu/GS catalysts in non-buffered (H₂) and buffered (H₂ + CO₂) runs at 30 °C.

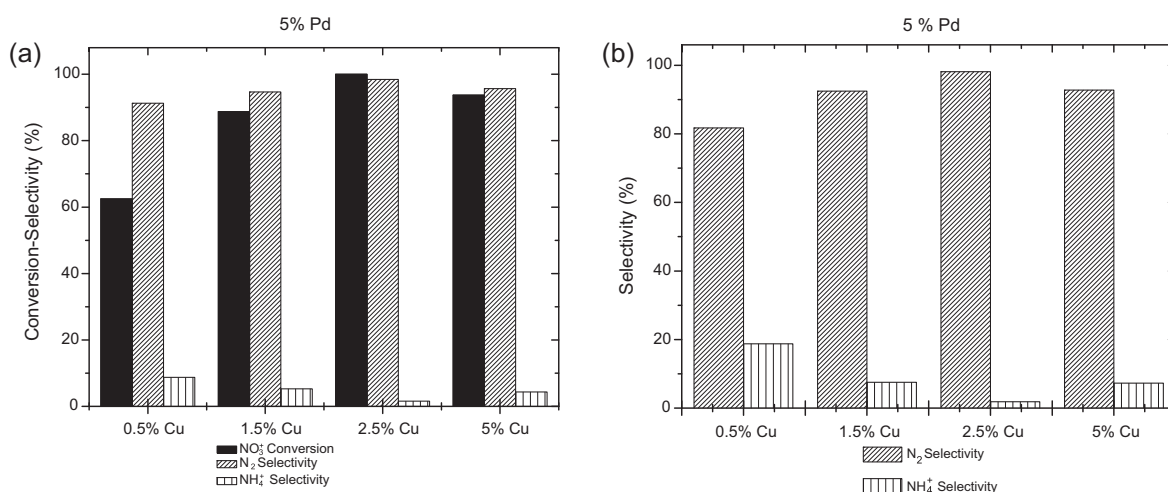


Fig. 5. Effect of Cu content of 5 wt.% Pd catalysts (GS-supported) on nitrate conversion and products selectivity (a) selectivity at reaction time = 8 h and (b) selectivity at 50% nitrate conversion at 30 °C.

[2], although the EDX analysis indicated that in all cases both Pd and Cu were homogeneously distributed throughout the metal particles. Lemaigen et al. [16] proposed that nitrates were reduced to nitrites on Pd–Cu centers, while nitrites were reduced on Pd centers. However, Yoshinaga et al. [2] indicate that not all Pd centers have the same reducing capacity. Pd centers located in the edges and corners of the microcrystals of Pd have a high capacity for hydrogenation, which favors reduction of nitrite up to ammonia. Moreover, N₂ was reported to be mainly formed in the Pd centers

located on the terraces of the microcrystals of Pd, because they have a milder hydrogenation capacity. By adding Cu to Pd microcrystal, this tends to be located at the edges and corners, providing a deactivation of the more reducing Pd and consequently it favors the selectivity towards N₂. However, as the Cu content is increased, the behavior is reversed and the selectivity towards ammonium increased. In this case Cu is placed on the entire surface of Pd microcrystals and Pd active centers can be separated from each other by Cu, thereby nitrite molecules adsorbed on the active centers are also separated, which leads to the formation of ammonia due to the difficulty in recombination of the N atoms to form N₂. TEM of 5Pd–2.5Cu/GS after reaction was carried out in order to study the possible modifications in nanoparticle size and/or dispersion. No significant variations were observed in these parameters after the reaction, only a slight increase in average diameter and decrease in dispersion (10%) was observed, suggesting a good stability of the catalyst in long-term application.

In a second series of experiments the influence of the Pd/Cu mass ratio of the catalysts was studied by fixing the Cu content at 2.5 wt.%. As it is shown in Fig. 7, a significant improvement of nitrate conversion was observed when increasing the Pd loading. The selectivity to N₂ decreased slightly in favor of ammonium when increasing the Pd loading for both at reaction time 8 h and at 50% nitrate conversion. Nevertheless, N₂ remained by far the main product within the range of Pd loading tested (1–5 wt.%). In the literature it has been

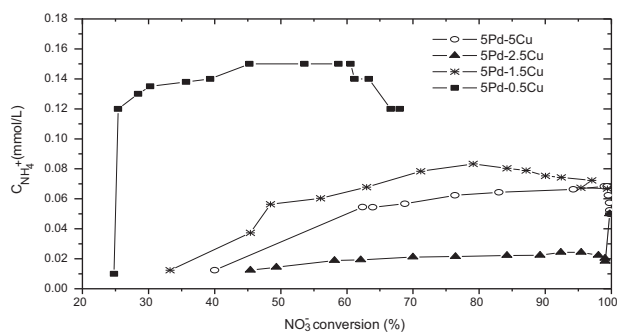


Fig. 6. Nitrate conversion versus NH₄⁺ concentration, fixing the Pd content in 5 wt.% in catalysts based in grape seeds.

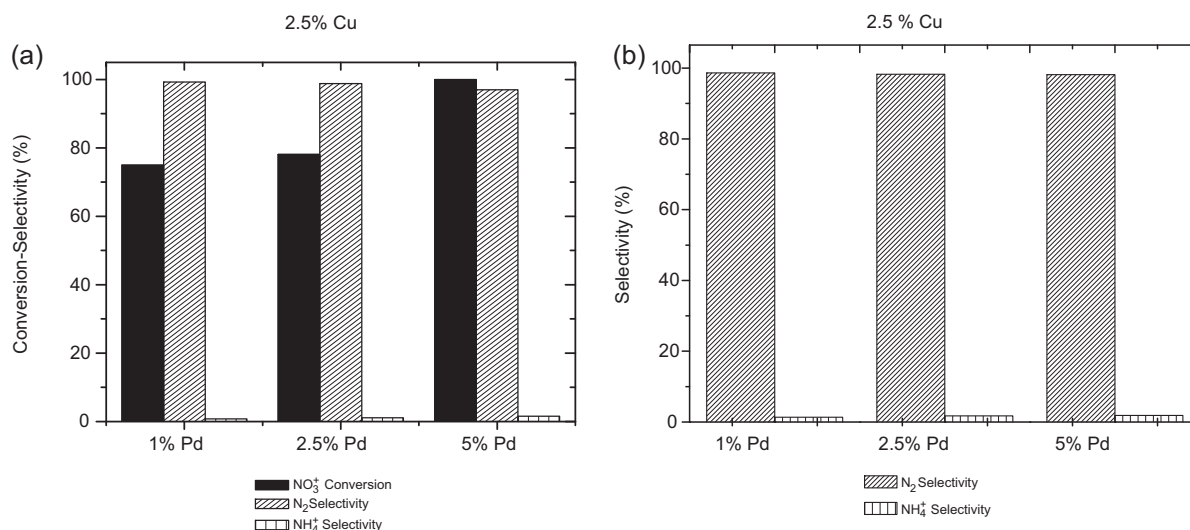


Fig. 7. Effect of Pd load (wt.%) in nitrate conversion and products selectivity (a) selectivity at reaction time = 8 h and (b) selectivity at 50% nitrate conversion with GS-supported catalysts with 2.5% Cu at 30 °C.

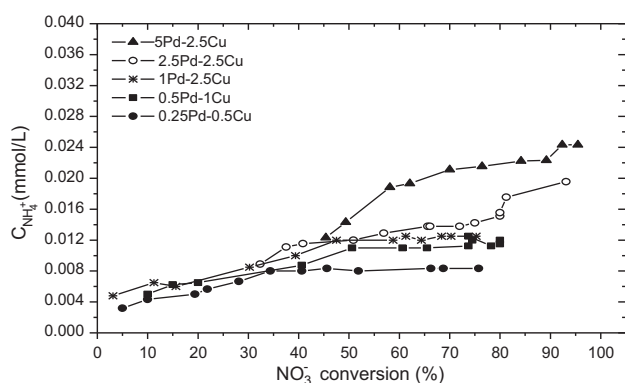


Fig. 8. Nitrate conversion versus NH₄⁺ concentration for catalysts based in grape seeds with different concentration of Pd and Cu.

described that ammonium is formed in Pd centers thus explaining the increase in selectivity to ammonium as the Pd loading increases [47,48]. A higher Pd loading is associated to an increase of the mean particle size as observed by TEM (see Table 3).

Different experiments were also carried out at constant Pd/Cu mass ratio (2) and varying the total metal (Pd + Cu) load from 0.75

to 7.5 wt.% (Fig. 8). Slight differences in nitrate conversion were found, but selectivity towards ammonium increased slightly (from 1% to 3.5%) with the metal loading. TEM characterization showed that decreasing the Pd load increased dispersion and gave rise to smaller particle size (Table 3).

3.3. Bimetallic Pd–Sn and Pd–In catalysts

We have tested two bimetallic catalysts of Pd (5 wt.%) with Sn and In (2.5 wt.%) as promoting metal for the sake of comparison with the 5Pd–2.5Cu/GS catalyst. Recent studies have claimed that Pd–Sn and Pd–In catalysts could be as active as Pd–Cu ones [48,49]. As can be seen in Fig. 9, 5Pd–2.5Cu/GS shows a higher activity than the Pd–In and Pd–Sn catalysts, this last being the one yielding the lowest nitrate conversion.

Significant differences were observed in the selectivity towards N₂, which is higher with the Pd–Cu catalyst. These results are not in agreement with the general trend indicated in the literature, where Sn has been claimed as a better promoter in terms of selectivity towards N₂ [30,38,50]. TEM yielded high nanoparticle sizes and low dispersion values with catalysts based on Cu and Sn (Table 3). An agglomeration of the metals is essentially observed owing to the high content of Pd in these catalysts. Therefore, different

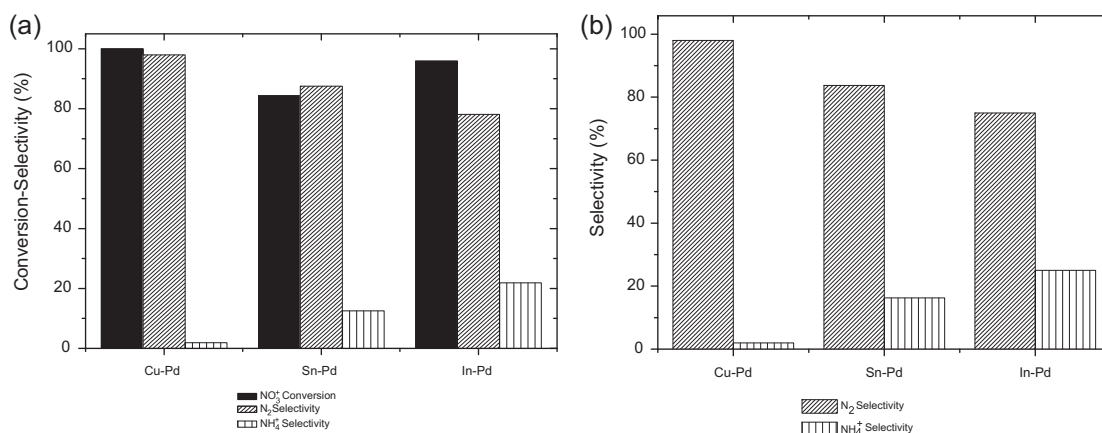


Fig. 9. Comparison of GS-supported bimetallic Pd (5 wt.%) catalysts with Cu, Sn and In (2.5 wt.%) (a) selectivity at reaction time = 8 h and (b) selectivity at 50% nitrate conversion at 30 °C.

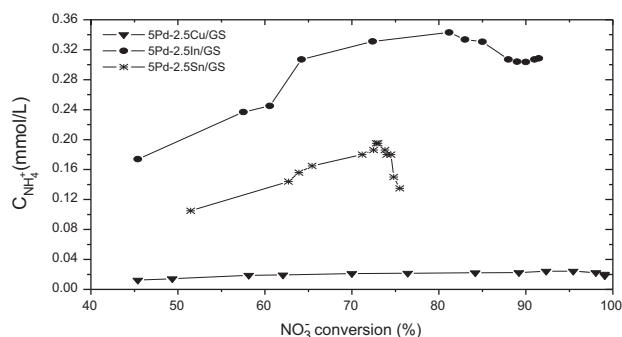


Fig. 10. Nitrate conversion versus NH_4^+ concentration for Pd–Cu, Pd–Sn and Pd–In catalysts.

catalytic behaviour may be attributed to the different metal–support interactions expected (Fig. 10).

4. Conclusions

Different activated carbon supported metal catalysts have been tested in aqueous-phase nitrate reduction, showing the relevant role of the support used. Pd–Cu catalyst prepared by chemical activation of grape seeds with phosphoric acid showed a higher nitrate removal activity and the absence of nitrite among the reaction products. Moreover, the selectivity towards ammonium was also lower. The chemical composition of the support can be considered as responsible for this behavior since it is able to provide buffering effect. Control of pH through CO_2 bubbling was only beneficial in the case of the catalyst prepared with a commercial activated carbon of high pH value of the slurry. The concentration of promoting metal seems to affect significantly the catalytic performances. Grape seeds based catalysts with 2.5 wt.% Cu and lower than 5 wt.% Pd contents satisfied European Standards for drinking water for the treatment of water with a nitrate concentration of 100 mg/L. Among the catalysts tested, Cu was the most adequate promoting metal when selectivity towards ammonium was considered.

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